



# Structural features, thermal behavior and biological activities of two new organically templated (Co<sup>II</sup>, Ni<sup>II</sup>) sulfates



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## ABSTRACT

The present paper undertakes the study of two new compounds with similar general formula (C<sub>6</sub>H<sub>9</sub>N<sub>2</sub>)<sub>2</sub>[M<sup>II</sup>(H<sub>2</sub>O)<sub>6</sub>](SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O with M<sup>II</sup> = Ni (1) and Co (2). In this context 1 and 2 are synthesized and characterized by single-crystal X-ray diffraction which revealed that these phases are centrosymmetric and crystallize, respectively, in triclinic and monoclinic symmetries. The thermal properties of both complexes are investigated as well as the IR spectroscopic and in vitro biological activities. The changes in geometry between these two complexes and intermolecular interactions such as hydrogen bonding and π···π stacking arrangement are discussed. Then, the cohesion between the amine cations, the inorganic parts and the free water molecules is performed via several types of hydrogen bonding forming interesting structural patterns. The pyridinium cations are aligned with each other in a face-to-face manner. The interlayer space is filled with aromatic amines that form chains through π···π interactions. The interlayer distances are 13.213 and 12.615 Å for 1 and 2, respectively. These materials were evaluated for their in vitro antibacterial activity against *Escherichia coli*, *Salmonella enterica*, *Bacillus subtilis*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Micrococcus luteus*. The ligand and its metal complexes have been also screened for their antifungal activity, using agar disc diffusion, against *Aspergillus niger*, *Saccharomyces cerevisiae* and *Candida albicans*. In addition, the antioxidant activities of the complexes were also investigated through scavenging effect on DPPH radicals, total antioxidant activity and reducing power.

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## 1. Introduction

The design and synthesis of hybrid complexes have attracted great attention in the fields of inorganic and coordination chemistry [1]. Therefore, it extends the range of designing new solids with desired physical and chemical properties [2]. Such as, the supramolecular compounds which exhibit a wide range of technological and industrial applications [3–6]. The main idea in development of the hybrid materials is to take advantage of the best properties of each component that forms a hybrid, trying to decrease or eliminate their drawbacks getting in an ideal way a synergic effect; that results in the development of new materials with new properties. The bonding in these materials is just as diverse as their structures, with covalent, ionic, and coordination bonds, hydrogen bonding, van-der Waals (vdW) forces, and π···π

stacking being observed in a single compound. Furthermore, hydrogen bonding between the organic cations and the metal layers is an important issue in understanding the hybrid organic-inorganic materials, which influences both the alignment and spacing of the nearest-neighbor metal sheets or chains. Unfortunately, despite some recent progress, the ability to predict and control the supramolecular assembly of molecules remains an elusive goal, and much more work is required to understand the intermolecular forces that determine the patterns of molecular packing in the solid state. Metal complexes may constitute one such possible class exhibiting biological activities [7–10]. Therefore, we have already drawn attention [11] to the strong relationship between metals or their complexes, and antibacterial [12], anti-tumour [13], and anticancer [14] activities. To the best of our knowledge, complexes in this report have never been explored for their antibacterial, antifungal and antioxidant activities. Therefore, this study opened the doors to develop such supramolecular materials that could be used to treat the diabetes, the anti-cancer and the anti-alzheimer.

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In the field of our investigations in the organic-inorganic hybrid materials, we report, herein, the chemical preparation, the spectroscopic characterization, the thermal behavior, the biological activities and the crystallographic description of two hybrid frameworks metal sulfates templated by 2-amino-6-methylpyridinium.

## 2. Materials and methods

### 2.1. Materials

In order to obtain crystals of high quality, purification of starting materials was found to be an important step and hence the re-crystallized salts were used for the growth of crystals of studied materials. All chemicals and solvents were purchased from Sigma-Aldrich and it was further purified by repeated re-crystallization process for three times using de-ionized water as the solvent.

### 2.2. Synthesis

Synthesis of compound **1**,  $(C_6H_9N_2)_2[Ni(H_2O)_6](SO_4)_2 \cdot 2H_2O$ : one mmol of Nickel(II) sulfate hexahydrate,  $NiSO_4 \cdot 6H_2O$ , and two mmol of 2-amino-6-methylpyridine,  $C_6H_8N_2$ , were each dissolved in 10 ml of distilled water. The Ni(II) salt solution was then added slowly to the ligand solution. The pH of the resulting solution was adjusted between 2 and 3 by dropwise addition of concentrated sulfuric acid  $H_2SO_4$  until the solution becomes clear. This later left for slow evaporation at ambient conditions. After a few days, green block crystals were harvested and characterized through single crystal X-ray diffraction.

Synthesis of compound **2**,  $(C_6H_9N_2)_2[Co(H_2O)_6](SO_4)_2 \cdot 2H_2O$ : one mmol of Cobalt(II) sulfate heptahydrate,  $CoSO_4 \cdot 7H_2O$ , and four

mmol of 2-amino-6-methylpyridine,  $C_6H_8N_2$ , were each dissolved in 10 ml of distilled water. The resulting solution was then added to an aqueous solution of sulfuric acid (initial and final pH: 2, 3) and stirred for 30 min. After agitation, the solution was left to slowly evaporate at room temperature. Pink block crystals suitable for X-ray structure analysis formulate and remain stable under normal conditions of temperature and humidity.

### 2.3. Single-crystal X-ray diffraction

Details of crystallographic data collection and refinement parameters for complexes **1** and **2** are given in Table 1. Single crystals of dimensions  $0.37 \times 0.31 \times 0.24$  (**1**) and  $0.50 \times 0.45 \times 0.35$  (**2**) mm, were mounted onto glass fiber and cooled to low temperatures. Data were performed, respectively, on a Kuma KM-4-CCD and Xcalibur Ruby diffractometers with graphite monochromatized  $MoK\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), using an Oxford Cryosystems cooler. Data collection, cell refinement, data reduction and analysis were carried out with CrysAlisPRO [15]. Analytical absorption correction was applied to the data with the use of CrysAlisRED [15]. Structures were solved with direct methods using SHELXS-97 [16] and refined by a full-matrix least squares technique with SHELXL-97 [16] with anisotropic thermal parameters for all non H-atoms. The aqua H atoms were located in a difference map and refined with O–H distance restraints of  $0.85(2) \text{ \AA}$  and H–H restraints of  $1.39(2) \text{ \AA}$  so that the H–O–H angle fitted to the ideal value of a water molecule. Hydrogen atoms bonded to C and N atoms were positioned geometrically and allowed to ride on their parent atoms, with C–H =  $0.95 \text{ \AA}$  and N–H =  $0.88 \text{ \AA}$ . All figures were made using DIAMOND program [17].

**Table 1**  
Crystallographic data and structure refinement parameters for compounds **1** and **2**.

Structural parameter	Compound 1	Compound 2
Formula	$(C_6H_9N_2)_2[Ni(H_2O)_6](SO_4)_2 \cdot 2H_2O$	$(C_6H_9N_2)_2[Co(H_2O)_6](SO_4)_2 \cdot 2H_2O$
Formula weight ( $g \text{ mol}^{-1}$ )	1226.52	1226.96
Temperature (K)	100 (2)	100 (2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P 2_1/c$
a ( $\text{\AA}$ )	7.3606 (18)	25.231 (6)
b ( $\text{\AA}$ )	13.213 (3)	13.844 (3)
c ( $\text{\AA}$ )	13.897 (3)	14.728 (4)
$\alpha$ ( $^\circ$ )	106.72 (2)	90
$\beta$ ( $^\circ$ )	105.03 (2)	103.46 (2)
$\gamma$ ( $^\circ$ )	98.69 (2)	90
V ( $\text{\AA}^3$ )	1212.4 (5)	5003 (2)
Z	2	8
Diffractometer	Kuma KM-4-CCD	Xcalibur, Ruby
Programs system	SHELXL-2013 and SHELXS-97	SHELXL-2013 and SHELXS-97
Absorption correction	Analytical	Analytical
$\rho_{cal}$ ( $g \text{ cm}^{-3}$ )	1.680	1.629
Crystal size ( $mm^3$ )	$0.37 \times 0.31 \times 0.24$	$0.50 \times 0.45 \times 0.35$
Crystal color/shape	GREEN, BLOCK	PINK, BLOCK
$\mu$ ( $mm^{-1}$ )	1.050	0.932
$\theta$ range (deg)	$\theta_{min} = 2.87, \theta_{max} = 36.71$	$\theta_{min} = 3, \theta_{max} = 36.81$
hkl range	$-12 \leq h \leq 9$ $-19 \leq k \leq 21$ $-23 \leq l \leq 23$	$-36 \leq h \leq 41$ $-22 \leq k \leq 23$ $-19 \leq l \leq 24$
No. of reflection collected	9162	20448
No. of independant reflection	7660	16550
F (000)	644	2568
R1	0.0373	0.0664
wR2	0.1098	0.1524
Goof	1.132	1.253
No. param.	321	671
Transmission factors	$T_{min} = 0.685; T_{max} = 0.737$	$T_{min} = 0.634; T_{max} = 0.722$
Largest difference map hole	$\Delta\rho_{min} = -0.533, \Delta\rho_{max} = 0.856$	$\Delta\rho_{min} = -0.939, \Delta\rho_{max} = 1.313$

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